JPRS Report

Science & Technology

Japan

PROCESSING FOR CREATION OF NEW MATERIALS

SCIENCE & TECHNOLOGY
JAPAN

PROCESSING FOR CREATION
OF NEW MATERIALS

[Public Seminar on Processing for Creation of New Materials held 23 Apr 91 in Tokyo, sponsored by the Science Council of Japan]

CONTENTS

New Ingot Iron, Iron Alloy Processing

[Article by Hiroyuki Katayama, Central Research Headquarters, Nippon Steel Corp.]

[Text] **1. Introduction**

This report will deal with the ingot processing in a broad sense, or the process between raw materials and solidification as related to iron and iron alloy processing. The ingot process is related to the "materials" through "the quality (components)" and "the cost of production." Because of the large quantity produced, iron and iron alloys have a great effect on society, and at the same time need to respond to the requirements from society, such as concern for the environment and waste disposal. This relationship is shown in Figure 1.

Almost nothing is impossible now in terms of ingot steel quality, as long as good materials are selected and the number of available processes are increased by doing so. Overcoming this contradictory relationship is the primary task to be accomplished in the area of processing. In the quest for cost reduction, social requirements are a strong restraint. Overcoming this contradictory relationship is the second task.
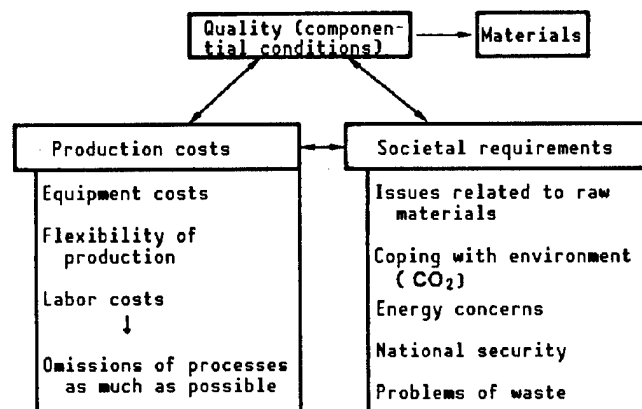

Figure 1. Relationship Between Materials and Ingot Processing

From the above standpoint, I would like to explain the state of recent technological developments in the field of iron smelting and refining and iron alloy production, and comment on the future direction of iron and iron alloy ingot processes.

2. Current Ingot Processes and Problems

Current mass-production ingot processes are the "blast furnace-converter method" using ore and coal as main materials, and the electric steelmaking process using scrap as a major material. Tasks to be done for the former method today include reduction of the number of processes and increase of the degree of freedom of choosing the raw materials and the production volume. As for the latter method, how to cope with the problem of impurities accompanying the scrap is the issue. Meanwhile, there is a problem of increased imports of iron alloy used for component adjustment, because Japan, with its high electricity charge, is in an economically disadvantageous position to produce iron alloy by the electric furnace method. Although these issues are not very serious problems now, as efforts for improvement have been made in each process, development of a new process should begin by resolving these issues.

3. New Ingot Processing of Iron Alloys and Iron by Melting Reduction

<The Aim of Melting Reduction and the Principle of the Melting Reduction Process Using Large Amounts of Slag>

Melting reduction is originally aimed at dissolution and reduction of materials, such as ore and coal, omitting preparation processes as much as possible. One of the reasons why melting reduction has not been put to practical use, even though many attempts have been made, is that efficient generation of heat by combustion and a reducing reaction could not be made to coexist. This problem has been solved by a smelting method (Figure 2)[1] using a large amount of slag, while shutting off metal bath agitated in an oxiding atmosphere. This method was made possible only after a method of controlling slag foaming was found.[2] Its features include higher combustion of the atmosphere (secondary combustion; 40~60 percent), and restrained generation of dust during slag reduction. Moreover, a method has been developed under which powdered ore can be used without agglomeration.[3]

Figure 2. Image of Interior of Furnace for Large Slag Quantity-Type Melting Reduction

<Melting Reduction Method as a Production Method of Alloy Iron>

The New Refining Key Technology Research Cooperative has conducted experiments to produce high-carbon ferrochrome from chromium ore by the above method up to the scale of 2t/h. Ferrochrome produced this way has less S, Si, and N than that produced by an electric furnace, and can be used more easily for
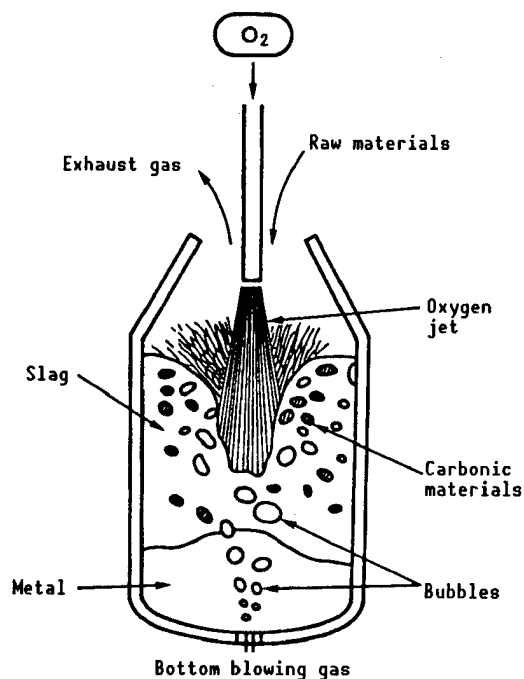
2

stainless steel making, for example. Furthermore, a method to produce low-P products has been developed. In addition, the chromium concentration of the discharged slag can be lowered to less than 0.5 percent, which is another feature of the melting reduction method.[4]

<Melting Reduction Method as a Production Method of Pig Iron>

It has been proved that the above method can be scaled up as a method of reducing iron ore by using a large converter.[2] Regarding the pig iron components of the product, there is a possibility that a feature, which blast furnace pig iron does not have, can be created by lowering P. However, it was pointed out that there were some problems if coal, one of the combustion materials, was used as is done in a melting reduction furnace.[5,6] Therefore, it seems that whether this method will be able to completely replace the blast furnace, among other applications of the melting reduction method, largely depends on the technological development of preliminary coal treatment and preliminary ore-reduction methods.

4. Problems of High-Purity Refining Technology of Ingot Steel and Use of Scrap

After ingot pig iron came the combined processes of "converter-ladle refining," in which the impurities of ingot steel, such as C, N, S, P, and O, can be reduced to a low level (Figure 3).[7] However, if scrap is used as a source of iron, there is a problem of impurities, such as Cu and Sn, being mixed in. In light of the efforts to increase the usage rate of scrap in an attempt to reduce CO_2 generation, technology to control the impurity concentrations of ingot steel must be developed. Elimination of impurities in ingot steel, however, is not easy, and an effective and practical method, is yet to be found. Under the circumstances, removal of Sn by utilizing the above method of melting reduction was reported,[8] suggesting a rational combination of melting reduction and scrap dissolution.
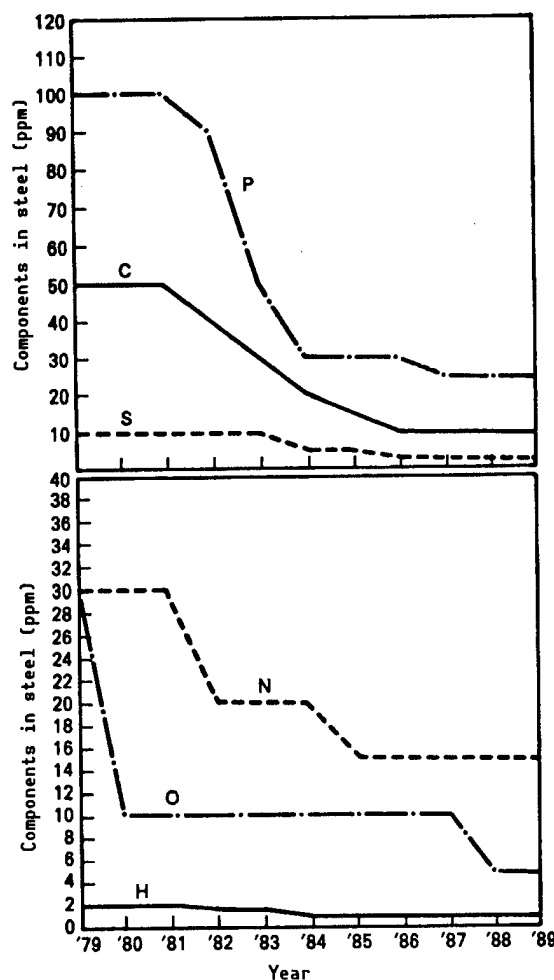
Figure 3. Trend of Results of Ingot Steel Purification by "Converter-Ladle Refining"

5. Outlook for Future Ingot Processing

Adachi suggested a concept shown in Figure 4 as a future crude steel-production system capable of withstanding economic fluctuations.[9] According to the concept, while the ratio of blast furnace method will be reduced to 50 percent and the electric furnace method will maintain the current ratio of 30 percent, the new melting reduction method will capture a 20 percent share. This clarification of the direction of future changes bears great significance, although it appears that the timing of transition will depend on future technological progress and the change of external conditions to a large extent. It is desired that ingot systems will shift swiftly in a direction which will turn out to be right in the long run, based on and rationally combining joint research such as "ferrochrome melting reduction,"[4] "iron melting production,"[10] and "New Steelmaking Forum," and the results produced by the Organization for Joint Research on Steel.
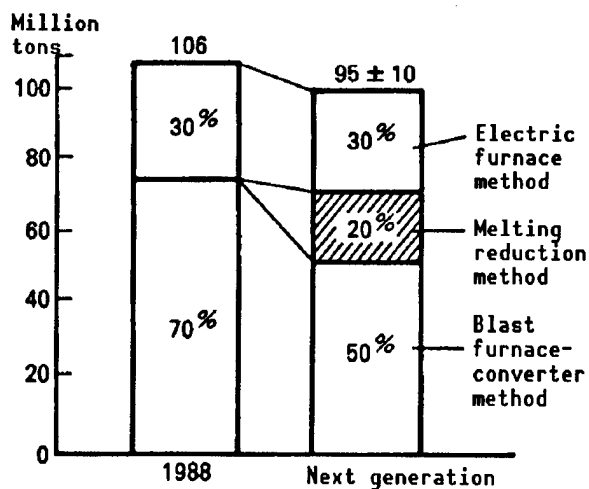
Figure 4. Crude Steel Production System Capable of Withstanding Economic Fluctuations

6. Conclusion

Much research is being conducted on ingot processing of iron and iron alloys in an attempt to manufacture "products that fulfill the compomential conditions required as a material" at "a low cost achieved by reducing the number of processes as much as possible," while "responding to social needs." I have discussed the present state and future outlook of melting reduction research.

References

1.   Fujita, et al., IRON AND STEEL, Vol 74, 1988, p 680.
2.   Matsuo, et al., Ibid., Vol 76, 1990, p 1876.
3.   Kuwabara, et al., CAMP ISIJ, Vol 3, 1990, p 111.
4.   Katayama, et al., IRON AND STEEL, Vol 76, 1980, p 1855.
5.   Matsuo, et al., Ibid., p 1879.
6.   Katayama, CAMP ISIJ, Vol 4, 1991, p 36.
7.   Shima, IRON AND STEEL, Vol 76, 1980, p 1765.
8.   Katayama, et al., CAMP ISIJ, Vol 3, 1990, p 1185.
9.   Adachi, Y., Proceedings of Sixth IISC, Vol 5, p 248
10. Tanaka, et al., CAMP ISIJ, Vol 3, 1990, p 1069.

High-Purity Metal Refining

[Article by Hiroshi Kimura, professor emeritus, Tohoku University, professor at Kanagawa University, and advisor, Nissin Steel Co.: "High-Purity Metal Refinery in Ultrahigh Vacuum"]

[Text] 1. Introduction

Recently, metals of high purity are attracting increased attention. There are a variety of means of high-purity refining of metals, out of which a method most suitable for a particular metal of targeted purity may be selected. Utilization of ultrahigh vacuum began about 25 years ago in the laboratory, and iron was successfully refined from a starter material of rather high purity sold on the market, even though purification of iron at higher than 99.999 percent was considered difficult. The method employed was a combination of ultrahigh vacuum and electron beam floating zone melting. The electron beam floating zone method at normal vacuum has an even longer history, and in fact has been used to refine metals with a high melting point for about 30 years.

Utilization of the method in ultrahigh vacuum has enhanced the purity further. Today's lecture is based on my experience refining molybdenum and iron during my tenure at Tohoku University, which succeeded owing to the cooperation of Suezawa, Matsui, and Takagi, and the results of iron purification recently carried out by Nakoshi's group at the New Materials Laboratory of the Nissin Steel Co.

I will begin by explaining that I am specialized in lattice defects and mechanical characteristics of metals, and refining per se is not my specialty. Once I obtain metals of desired purity, I devote all my efforts to examination of their characteristics. So I hope you will forgive me for the somewhat incomplete contents of my research on refining.

2. Outline of Ultrahigh Vacuum Electron Beam Floating Zone Melting Method

Metal refining by vacuum melting has been known for years and has been used widely for industrial purposes. Under this method, metals are refined by evaporating gas impurities and elements at high vapor pressure. The most prevalent is its application under 10^{-3}Pa or lower degree of vacuum. Ultrahigh vacuum refers to 10^{-7}Pa or higher degree of vacuum. The refining effect by evaporation is facilitated if metals are melted in such vacuum. Equally important is the influence of the composition of residual gas. Most of the residual gas in an ultrahigh vacuum range is hydrogen, and the partial pressure of oxygen is very low. Ultrahigh vacuum is, so to speak, an atmosphere of extremely weak reducibility. We should not assume that the pressure went down while the composition of the air remained the same.

In refining high-purity metals, impurities in the metals must be removed, and at the same time contamination from the crucible circumference must be prevented. In ultrahigh vacuum, we do not have to be concerned about contamination from the atmosphere because of the low partial pressure of oxygen works to our advantage. During melting, contamination from a crucible should be given the most attention. However, the floating zone melting method does not require the use of a crucible. The heating method in this case may be high-frequency induction heating, but electron beam heating is also effective when metals with a high melting point are being refined. Even if these methods are used, contamination cannot be prevented completely. For example, our group used filaments of tungsten wire and a tantalum electron gun, several centimeters in diameter, covering the filaments to melt a round rod 5 mm in diameter. Even though the sample rod did not contact the filaments or the tantalum board, the refined iron was contaminated with several parts per million of tantalum and tungsten. Moreover, it should be borne in mind that there is a danger of cross contamination if more than one kind of metal is refined in the same equipment, as salt metals are deposited on the inner wall of the vacuum chamber.

Because ultrahigh vacuum electron beam floating zone melting equipment is not readily available yet, one would have to have such equipment custom made. As various improvements have been made, such equipment is now much more convenient to use compared to the equipment we purchased 20 years ago. (Our group takes a little pride in its contribution to the improvements.) Nevertheless, it takes some time to acquire the skills necessary to use ultrahigh vacuum equipment.

When the floating zone melting method is used, there is a limit on the diameter of the metal rod to be refined. If contamination from a crucible does not matter, one may not have to employ the floating zone melting method. And if the subject metal does not have a very high melting point, internal high frequency induction heating rather than an electron beam will do.

3. Determination of Purity of High-Purity Metals

At present, it is impossible to accurately determine purity higher than 99.999 percent by analyzing all impurities contained in a sample. As far as metals are concerned, it is convenient to indicate their purity by residual resistance ratio (RRR), a figure calculated by dividing the value of electrical resistance at high temperature (273 K or a constant temperature near room temperature) by the electrical resistance at low temperature (usually 4.2 K). Because most of the electrical resistance at very low temperature is attributed to dissolved impurities, residual resistance ratio is in inverse proportion to the concentration of the dissolved impurities. When it comes to iron, which has resistance attributable to strong magnetism at low temperature, measurement is made while a magnetic field is applied and the resistance is held down to a constant and minimum value. In this case, the measured result is expressed as RRR.

4. Handling After Refining

Even though many people are very enthusiastic about refining and acquisition of materials of high purity, they seem to be surprisingly unconcerned about lowering of purity through later handling. The same degree of caution should be exercised in handling metals of high purity as in refining them, to prevent contamination.

Processing should always be done at room temperature, while surface contamination due to the processing is removed frequently, and hydrogen treatment should be applied at the last stage to eliminate contamination (mainly carbon). If metals of high purity are melted to produce alloys, attention should be given to the purity of the alloy elements to be added, and they should be melted by the same method or under as clean conditions as they were refined. There are many cases where hard-earned metals of high purity are contaminated by careless melting.

5. Examples of Refining

The ultrahigh vacuum electron beam floating zone melting method began to be used in the latter half of the 1960s, and has a rather long history of application in the laboratory. The method was first applied to tantalum. Although the main objective was to decrease the gas impurities of tantalum, which contains a large amount of dissolved gas, the overall purity was improved. In fact, a sample which was considered to be purer than 99.999 percent was produced. This contributed to research on lattice defects. The Max Planck Research Institute of Germany is applying the method to niobium to produce samples for basic research. Our group at the Research Institute for Metals applied the method to molybdenum and iron, and the New Materials Laboratory of Nissin Steel is refining iron by this method.

6. Conclusions

Application of ultrahigh vacuum technology to high-purity refining of metals is in a state where out of necessity researchers on lattice defects successfully utilize the technology in combination with the electron beam floating zone melting process to refine and produce samples of required purity. However, systematic study on the mechanism of refining and the limit of application is still inadequate. Future research should investigate combining ultrahigh vacuum technology with other refining methods suitable for mass production so that the technology can be applied to an increasing number of metals.

References

1.   Takaki, S. and Kimura, H., SCRIPTA METALL., Vol 10, 1976 pp 171, 1095.

2.   Nakoshi, T., Muraki, K., Sasaki, Y., and Sakakura, A., NISSIN STEEL TECHNICAL REPORT, Vol 63, December 1990 p 1.

Latest Powder Processing

[Text] 1. **Free Energy of Powder**

Powder has such special characteristics that justify its recognition as the fourth state (phase), rather than vapor, liquid or solid. Physically, it exhibits fluidity like a liquid and rigidity like a solid, depending on the conditions. Chemically it is active and sinters and solidifies at low temperature.

When trying to distinguish powder from the other three phases, the state of free energy of powder should be taken into account. Because each particle of powder is a solid, it is safe to assume that the free energy of the bulk is almost the same as that of a solid. The excessive free energy is attributed to its large surface area. The free energy of a solid, or a metal, for instance, is in the range of hundreds to thousands of ergs per square centimeter. This means that Fe powder of about 1 μm in grain diameter with surface energy of 10^3 erg/cm^2 is in a state of energy higher than Fe bulk by 50 J/mol.

The free-energy values of a solid phase and a liquid phase are equal at a melting point, Tm. The excessive energy value, against a solid phase, of a liquid phase which was supercooled to below Tm can almost be expressed as L x ΔT/Tm, with ΔT and L representing the degree of supercooling and latent heat, respectively. As the value of L of a metal is about RTm (R is a gas constant), it is understood that in the case of Fe (Tm $\approx$ 1800 K), the degree of supercooling, ΔT, necessary for the energy increase of the liquid phase by foregoing 50/mol is only about 6 K. by developing such rough estimation, it is assumed that the state of energy of about 10^{-6}cm (10 nanometers) ultrafine powder is, in the case of Fe, equivalent to the supercooling of about 300 K of the liquid phase. Supercooling of this magnitude is achieved only by a process known as the rapid solidification (RS) method of a liquid phase. RS is a method of producing amorphous metals. It means that as far as the free energy value itself is concerned, there should be a possibility of producing a

9

metastable phase of nonequilibrium by the solid—phase reaction of powder, provided that powder of about 10 nm can be obtained. So far, we have discussed the powder of pure substances. Regarding a mixture of powders of different substances, however, mixed free energy (or compound formation energy) generated by mixing of pure substances should be taken into consideration in addition to the surface energy.

2. Free Energy of Mixed Powder of Two Kinds of Elements

Consider the free energy made by mixing powders of elements A and B, by comparing the state of energy when these elements are mixed in an atomic order and form a solid solution, and when they produce compounds. Examples of four different alloy systems are shown in Figure 1. The datum in the figure, i.e., the line connecting 0, indicates the free energy value of the mixed powder. The differential of free energy between mixed powder containing the elements 50 percent each and a uniform mixed phase (liquid phase, fcc phase, bcc phase, etc.) is about +20 KJ/mol in an Ag—Fe system, and —20 KJ/mol in an Al—Fe system.

Figure 1. Relationship Between Free Energy of Mixing and Composition in Four Alloys

Positive energy of mixing suggests a tendency that the two kinds of elements repel each other and do not intermingle, and negative energy indicates high affinity. The figure of the energy differential, 10 KJ/mol, is rather large compared to the foregoing energy differential due to supercooling. By just mixing powders, energy differential larger than what the rapid supercooling (RS) method manages to achieve is generated. This is a major characteristic of powder.

3. Utilization of Excessive Energy of Mixed Powder: SHS (Self-Propagating High-Temperature Synthesis) and MA (Mechanical Ironing)

The free energy value of mixing could reach tens of KJ per mol, as discussed above. Most of this free energy can be considered as mixing enthalpy (heat of reaction). Although the mixing energy of the aforementioned Ag—Fe had a large positive value, many alloys have a negative value, and alloy systems, especially those that form intermetallic compounds, have a large negative figure, like the above case of Al—Fe.

Therefore, mixed powder is in the state of high energy. An intermetallic compound synthesis method, called SHS (self—propagating high—temperature synthesis), takes advantage of heat generation caused by release of the high energy of mixed powder. When mixed powder reacts and produces intermetallic compounds, a liquid phase may be formed temporarily if the heat of reaction is very high. However, the reaction is usually a solid—phase reaction, and therefore the rate of the reaction is slow for its large calorific power, and
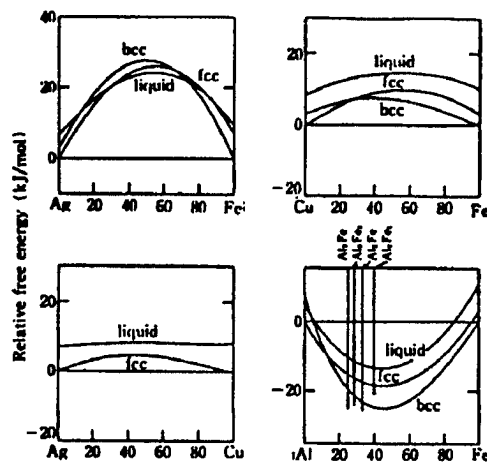
explosive reaction does not occur because a vapor phase is not involved. Compared with conventional melting and casting processes, this method enjoys many advantages in synthesizing intermetallic compounds with a high melting point. For example, a crucible is not needed, and the use of a heat source is no more than supplementary. Unlike SHS that releases high energy of mixed powder at once, MA (mechanical ironing) is a process of lowering energy gradually by kneading mixed powder mechanically for a long period of time and making an alloy structure in nonequilibrium state of energy. The essence of the mechanical kneading process is repetition of rolling and folding, the same as the principle of rice-caking making. This principle is illustrated in Figure 2. This process mixes the grains of different elements contained in the mixed powder into the dimensions of nanometers, and enables making an alloy by atomic diffusion in a solid phase at low temperature.

Figure 2. Principle of Mechanical Ironing Process
(If $a = 0.3$, thickness will be about $10^{-5} \times d_0$ after rolling and folding 10 times.)

4. Solidification Forming of Powder by Pseudo Hydrostatic Pressure: Pseudo-HIP

To use powder in a stable, metastable or nonequilibrium state produced by SHS, MA or RS, it must be molded by one method or another. HIP is a general, well known, hydrostatic pressure-molding method at high temperature. As heating is carried out in vapor of about 2,000 atm under the HIP, the operation efficiency is low, and strict safety control is required. A method that is attracting attention recently is a process of generating pseudo hydrostatic pressure by using sand (solid) as a pressure medium, and solidification forming under heated and vacuum conditions. Figure 3 illustrates this method. It is expected to be used more widely as a safe and simple powder-molding method. Producing materials by taking advantage of the unique state of energy of powder is a sintering method that also has been used widely. The characteristics of powder will be utilized more and more in the future, as various new processes are developed.
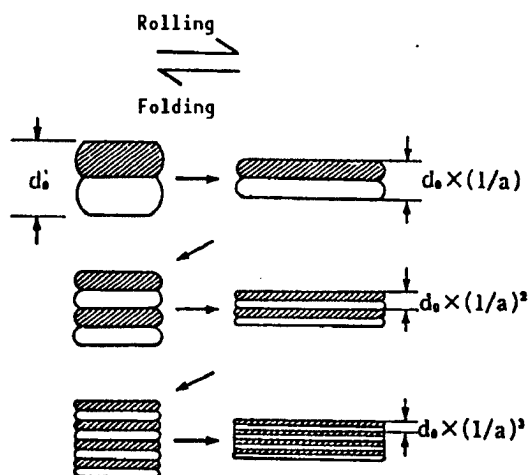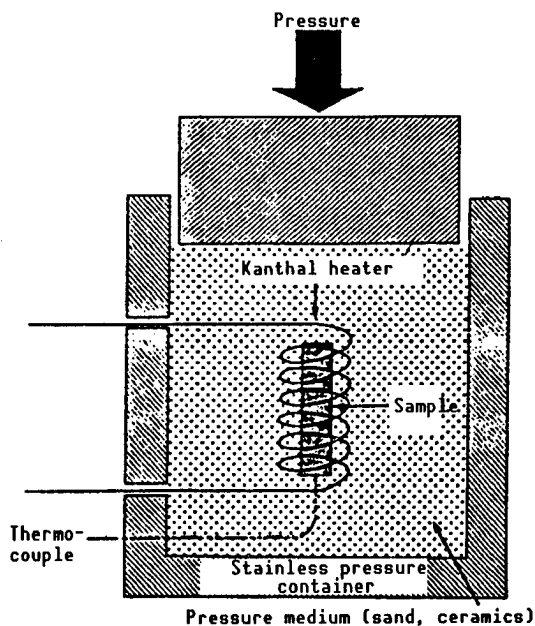

Figure 3. Schematic Diagram of Process by Pseudo-HIP

References

1. Shingu, H. and Ishihara, K., POWDER AND POWDER METALLURGY, Vol 37, 1990, p 78.

2. Shingu, H., CHEMISTRY, Vol 43, 1988, p 760.

3. Shingu, P.H., "Solid State Powder Processing," ed. by A.H. Clauser and J.J. deBarbadillo, TMS, 1990, p 21.

4. NIKKEI NEW MATERIALS, No 81, 1990, p 32; Ibid., No 83, 1990, p 63.

Ceramic Materials Processing

[Article by Kenji Morinaga, General Science and Engineering Department, Graduate School of Kyushu University]
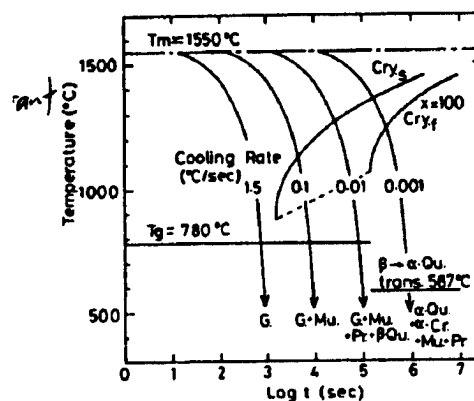
[Text] 1. Introduction

One of the basic technologies of dry smelting of metals is handling and heat control technology based on the physical properties and structures of high-temperature melt. The speaker has tried for the past several years to apply the basic technology to new materials processing by taking advantage of the accumulation of research on the physical properties and structures of slag. In this report, I would like to discuss 1) synthesis of oxide ceramics from melt, and 2) composition designing of oxide ceramics and glass in terms of the basicity of slag, among others. Diversified heat sources, including electron beam, can be used for oxides, to which induction heating cannot be applied, and this has made melt processing possible. This indicates that the bases of the technology are the cooling process and the CCT and TTT diagrams of steel. In addition, I would like to discuss the necessity of standard parameters for the composition of glass. It is said that there are tens of thousands of practical compositions of glass and 250,000 compositions have been studied. Furthermore, I would like to show that the basicity of slag may be the basis for such parameters.

Cry : Crystallization, S : start, f : finish, X : Crystallinity (%), trans.: transformation, Mu.: Mullite, Pr. : Protoenstatite, G. : Glass, Qu : Quartz.

Figure 1. CCT Diagram of Melt of Cordierite Composition During Solidification Process

2. Usefulness of CCT and TTT Diagrams

2.1 Cordierite

Cordierite has the characteristics of small coefficient of expansion and dielectric constant. Because incongruent

13

melting of cordierite occurs at about 1,345°C, it is difficult to produce fine ceramics made of single–phase cordierite. Figure 1 is the CCT diagram of melt of cordierite composition (2MgO·2Al₂O) in its solidification process. As shown in the figure, no matter what rate of continuous cooling is applied to the melt of cordierite composition, a cordierite phase does not crystallize. Figure 2 is a TTT diagram drawn by cooling the melt swiftly to a prescribed temperature and holding it at that temperature. Acknowledged cordierite phases are "low" cordierite at 1,673 K (1,400°C) and 1,623 and μ– and α–cordierite at 1,253 K and 1,223 K. During the transformation process from μ–cordierite to α–cordierite, plane defects and dislocation are

Figure 2. TTT Diagram of Melt of Cordierite Composition During Solidification Process

confirmed by transmission electron microscopy (TEM) observation. It was learned that the transformation was similar to the isothermal martensitic transformation of steel.[1]

2.2 Mica Ceramics

Mica ceramics containing glass as the matrix and dispersed mica are drawing attention as ceramics to which mechanical processing can be applied. Their properties depend on the grain diameter and the pattern of the mica crystals. Figure 3 is the TTT diagram of fluorine gold mica system($48.2SiO_2 \cdot 9.8Al_2O_3 \cdot 19.2MgO \cdot 7.4MgF_2 \cdot 6.7K_2O \cdot 8.7B_2O_3$). The composition of the melt was selected so that the rate of crystallization is slow, and the fine structure is easy to control. Fluorine gold mica crystallizes out at below 1,473 K. It crystallizes following spinodal decomposition–type phase splitting, especially below 1,253 K. The rate of crystallization of fluorine gold mica

Figure 3. TTT Diagram of Fluorine Gold Mica System

depends on the holding time and temperature. It reached 45 percent at temperatures higher than the phase–splitting zone, and was 20 percent within the formation region of the phase–splitting. Isothermal holding within the phase–splitting zone made it possible to control the grain diameter and pattern of fluorine gold mica crystals.
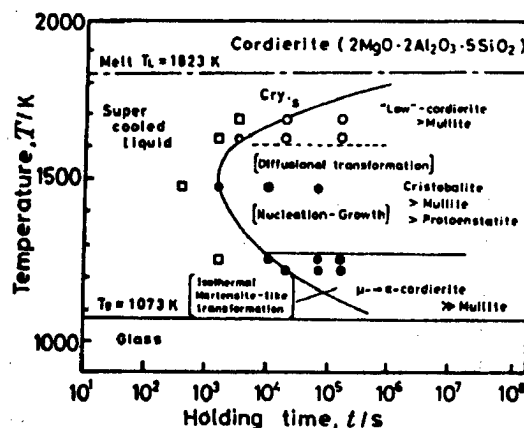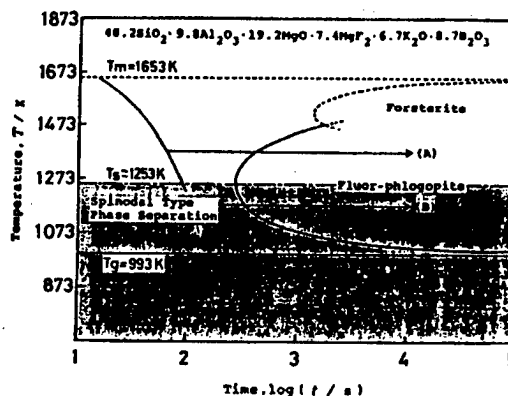
14

3. Composition Parameters of Oxide Glass Based on Slag Basicity

The basicity of slag is a composition parameter representing reactivity to the outside, which is important for removal of impurities at the time of metal smelting and refining. Also, when the subject is functional glass, it represents latent oxidation and reduction capability. Here, I would like to suggest a basicity parameter, pO value, I arranged the valency of transition metallic ions (M^n, M^{n+1}) in oxides and oxygen coordination numbers (CN) according to the following formulas:

$$M^n/M^{n+1} = f \text{ (amount and composition of } PO_2, T, M) \quad (1)$$

$$M(CN) = f \text{ (amount and composition of } M) \quad (2)$$

4. Conclusion

A method to control the crystalline phase and structure of oxide ceramics for melt processing by using CCT and TTT diagrams has been discussed. The author has a vision of developing a new processing method of oxide ceramics using melt by combining the key technologies of new heat sources, melt smelting and refining effects, casting, solidification structures, and thermal processing. Moreover, the author is trying to develop the concept of the basicity of slag and design the composition of functional oxide glass by the three dimensions of radius of ions, electronegativity, and polarizability.

$$Sn^{2+} + \tfrac{1}{2}O_2 \rightleftharpoons Sn^{4+} + O^{2-} \qquad \text{(Type R)}$$

$$Sn^{4+} + \tfrac{1}{2}O_2 + 2O^{2-} \rightleftharpoons (Sn^{4+}O_3)^{2-}$$
$$\text{(Type 0)}$$
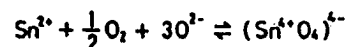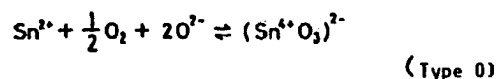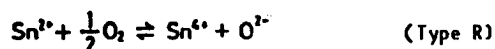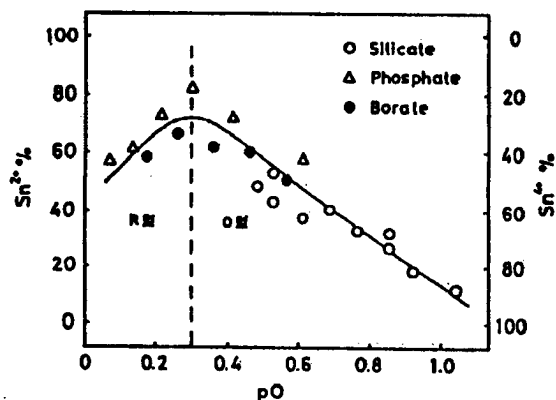$$Sn^{4+} + \tfrac{1}{2}O_2 + 3O^{2-} \rightleftharpoons (Sn^{4+}O_4)^{4-}$$

Figure 4. Relationship Between Valency and pO Value (10 mol% SnO was added to SiO_2, P_2O_5, and B_2O_3 type glasses prepared at various basicity (pO value)

References

1. Takebe, H. and Morinaga, K., "NIPPON KINZOKU GAKKAISHI, No 54, 1990, p 556.

15

New Glass Materials Processing

[Article by Takao Makishina, Materials Course, Engineering Department, Tokyo University]

[Text] 1. What Is New Glass?

Unlike ordinary glass such as window glass and bottle glass, new glass is a useful new material with new functions that play an important role in advanced science and technology. Table 1 shows the kinds of new glasses by function.[1] The new glasses include crystallized glass produced by applying thermal treatment, porous glass obtained by phase splitting and applying a number of chemical solutions, and composite materials made by compounding and incorporating SiC fibers and glass. One of the features of the new glasses is the wide variety of shapes possible including plates, tubes, fibers, rods, and bulks.

New glass technology is rapidly advancing, and the New Glass Forum, established by 170 firms including steel companies as a research organization for the domestic industry, is conducting aggressive research activities. The new Glass Forum studied what kinds of new glass is promising and, forecasted the size of the market in the year 2000. As a result, it estimated the market size at about ¥2 trillion, and identified new glass expected to be developed further. They are listed in Table 2.[1]

2. Characteristics of Glass

The general characteristics of glass are shown in Table 3.[2] These characteristics are best made use of in glass synthesis and processing, where the functions are given full play.

Table 1. Kinds of New Glass[1]

Functions	Examples of new glass

Optical functions
  Transmittancy
 	
  Fluorescent property
  Optical phase change
  Selective permeability
 	
  Acoustical-optical effect
	Optical fibers for communication
	Infrared-ray fibers
	Microoptical lenses
	Laser glass
	Glass for optical memory
	Heat-reflecting glass
	Solar cell cover glass
	Glass for light modulation/deflection

Electric and magnetic
functions
  Magnetooptical effect
  Electric insulation
 	
  Ionic conductivity
	
	Faraday rotation glass
	Electroluminescence substrates
	Liquid crystal display element substrates
	Solar cell substrates
	Ultra-ionic conductive glass

Thermal and mechanical
functions
  Low expansiveness
  High strength
 	
  Workability
	Zero-expansion crystallized glass
	
	Zero-expansion crystallized glass
	Fiber reinforced crystallized glass
	Oxinitride glass
	Machinable crystallized glass

Chemical and biofunctions
  Corrosion resistance
 	
  Adsorptiveness
 	
  Organism compatibility
	
	Glass for disposal of radioactive waste
	Crystallized glass for interior and exterior
	  of buildings
	Porous glass for enzyme and catalyst
	  carriers
	Glass for artificial bones and teeth and
	  crystallized glass

Table 2. Kinds of New Glasses Expected To Be Developed Further

(1) High-optical transmission infrared fibers (2) High-performance light radiation glass (3) Optical circuit new optical-element glass (4) Optoelectronic and electronic functional glass (5) Optoelectronic high-performance glass substrates (6) High-quality high-integration glass composite substrates (7) New high-strength glass (8) Porous glass of high chemical functions (9) New SEITAI functional glass (10) High-performance glass obtained by new production processes such   as sol-gel low-temperature synthesis

Table 3. Characteristics of Glass

(1) Roughly 90 kinds of elements are contained in glass, and there are a huge number of combinations. In other words, there are infinite kinds of glass. (2) Continuous alteration of glass properties is possible, and thus, materials designing is also possible. (3) Because the structure is indeterminate, it can be made into various shapes such as fibers, plates, and tubes. (4) The properties are isotropic, and there are no grain boundaries. (5) Alteration, such as crystallization and phase separation, is possible.

3. New Glass Processing

Glass synthesis methods include: 1) the high temperature melting method, 2) the vapor phase synthesis method, 3) the sol-gel method, etc. In some cases, glass is processed by thermal or chemical treatment and made into new glass. These methods will be further discussed below.

The high temperature melting method is a method to produce glass by literally melting raw materials at high temperature. Various measures have been contrived to obtain new glass by this method. A float method and a fusion process are employed to produce smooth, and nonalkali glass for liquid crystal displays and display boards. These methods take advantage of the smoothness of the free surface of melt or smoothness achieved by flowing glass melted on molten tin. Fluoride glass, an infrared permeable glass, is produced by melting fluoride materials in inactive vapor.

The vapor phase materials method is employed to make glass with no thermal expansion, to be used as glass for optical fibers and space telescopes. Under this method, oxides are produced through high temperature oxidating reaction by vaporizing new materials, including $SiCl_4$. It offers many advantages. For example, glass of ultrahigh purity can be obtained and glass with composition distribution, i.e., refractive index distribution, can be produced by precisely controlling the addition of metallic halide.

The sol-gel method is a process which goes through the states of sol and gel by chemical reaction of a material solution and then thermal treatment to produce glass bulks, coating films, and fibers. Products of this method include coating films of window glass, the heads-up display of automobiles and the high-purity silica glass fibers of the refractor of electric furnaces for LSI processing. This process is interesting because it is simpler than the vapor phase synthesis and vacuum and chemical deposition, and has the merit

18

that many kinds of elements can be used. Research on this method is progress-ing. Moreover, although there is a limit on the temperature of the thermal treatment, new hybrid materials can be created, because under this method it is possible to compound and incorporate functional organic molecules and inorganic substances on a molecular level.

References

1. "New Glass Survey Report, No. 1," edited by the New Glass Forum, 1986.

2. Takao Makishima, "Introduction to Functional Glass," Agune, 1984.

- END -

Foreign Broadcast Information Service (FBIS) and Joint Publications Research Service (JPRS) publications contain political, military, economic, environmental, and sociological news, commentary, and other information, as well as scientific and technical data and reports. All information has been obtained from foreign radio and television broadcasts, news agency transmissions, newspapers, books, and periodicals. Items generally are processed from the first or best available sources. It should not be inferred that they have been disseminated only in the medium, in the language, or to the area indicated. Items from foreign language sources are translated; those from English-language sources are transcribed. Except for excluding certain diacritics, FBIS renders personal names and place-names in accordance with the romanization systems approved for U.S. Government publications by the U.S. Board of Geographic Names.

Headlines, editorial reports, and material enclosed in brackets [ ] are supplied by FBIS/JPRS. Processing indicators such as [Text] or [Excerpts] in the first line of each item indicate how the information was processed from the original. Unfamiliar names rendered phonetically are enclosed in parentheses. Words or names preceded by a question mark and enclosed in parentheses were not clear from the original source but have been supplied as appropriate to the context. Other unattributed parenthetical notes within the body of an item originate with the source. Times within items are as given by the source. Passages in boldface or italics are as published.

SUBSCRIPTION/PROCUREMENT INFORMATION

The FBIS DAILY REPORT contains current news and information and is published Monday through Friday in eight volumes: China, East Europe, Central Eurasia, East Asia, Near East & South Asia, Sub-Saharan Africa, Latin America, and West Europe. Supplements to the DAILY REPORTs may also be available periodically and will be distributed to regular DAILY REPORT subscribers. JPRS publications, which include approximately 50 regional, worldwide, and topical reports, generally contain less time-sensitive information and are published periodically.

Current DAILY REPORTs and JPRS publications are listed in *Government Reports Announcements* issued semimonthly by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 and the *Monthly Catalog of U.S. Government Publications* issued by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

The public may subscribe to either hardcover or microfiche versions of the DAILY REPORTs and JPRS publications through NTIS at the above address or by calling (703) 487-4630. Subscription rates will be provided by NTIS upon request. Subscriptions are available outside the United States from NTIS or appointed foreign dealers. New subscribers should expect a 30-day delay in receipt of the first issue.

U.S. Government offices may obtain subscriptions to the DAILY REPORTs or JPRS publications (hardcover or microfiche) at no charge through their sponsoring organizations. For additional information or assistance, call FBIS, (202) 338-6735,or write to P.O. Box 2604, Washington, D.C. 20013. Department of Defense consumers are required to submit requests through appropriate command validation channels to DIA, RTS-2C, Washington, D.C. 20301. (Telephone: (202) 373-3771, Autovon: 243-3771.)

Back issues or single copies of the DAILY REPORTs and JPRS publications are not available. Both the DAILY REPORTs and the JPRS publications are on file for public reference at the Library of Congress and at many Federal Depository Libraries. Reference copies may also be seen at many public and university libraries throughout the United States.